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(19)


## (54) STABILIZATION OF PYRETHROIDS

(71) We, CPC INTERNATIONAL INC., a Corporation organised under the laws of the State of Delaware, United States of America, of International Plaza, City of Englewood Cliffs, State of New Jersey 07632, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved aqueous spray composition which is effective against both flying and crawling insects.

Much work has been done recently in attempts to prepare a synthetic insecticide having a combination of desirable biological and physical properties. It should, of course, exhibit high toxicity to insects but have very low mammalian toxicity. Also, it should be stable in a wide variety of formulations, but it should be degradable after application so as to leave no dangerous residues. At the same time, however, it should be persistently effective for more than a few days so as to eliminate the need for frequent applications.

The use of mixtures of known insecticides is not effective to attain these goals because those insecticides which are effective over a long period of time are thus effective because they are not degradable, i.e., they remain effective for too long a period of time and thus pose a serious ecological problem because of their possible ultimate ingestion by mammals and their accumulation and concentration in the fatty tissues of mammals. For this reason, insecticides such as DDT have been banned from general use and are not available. On the other hand, those insecticides which are non-toxic and whose use is therefore permitted around home and work areas, comprising essentially the pyrethroids, are not very persistent and require frequent, almost daily re-application.

Insecticide formulations are used in a wide variety of forms, including emulsified aqueous sprays, aqueous pressurized sprays, oil sprays, wettable powders, dustable powders, and oil based aerosols. The present invention deals only with aqueous pressurized sprays and emulsified aqueous sprays.

It is a principal object of the present invention to provide an aqueous insecticide spray composition which is effective both against flying insects and crawling insects.

It is also an object of the present invention to provide an aqueous insecticide spray composition which is degradable, but which at the same time provides relatively long-term protection against crawling insects.

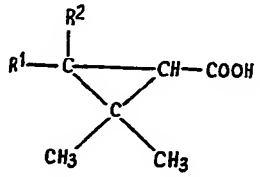
It is also an object of the present invention to provide such a spray composition which is effective both to flush out hidden insects and to kill them on contact.

The present invention accordingly provides an aqueous pressurized spray composition comprising from 0.20% to 2.0% by weight of a pyrethroid insecticide, from 0.05% to 2.0% by weight of an ortho-substituted phenol having from 10 to 60 carbon atoms per phenolic group, from 0.5% to 1.5% by weight of a non-ionic emulsifying agent, and from 30% to 50% by weight of a propellant. The weight ratio of pyrethroid insecticide to phenol preferably being from 1:1 to 5:1. Such composition is non-toxic and degradable, yet it is persistently effective over a period of 4—6 weeks. Moreover, it has good knockdown and kill against flying

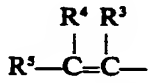
insects and good flushing characteristics and kill against crawling insects such as cockroaches. Thus, it serves the purposes both of a space spray and a baseboard spray and, because of the low toxicity of the insecticide component, it can be used for disinfection in household and work areas.

The insecticide may be any of the esters of chrysanthemic or pyrethric acid, e.g. allethrin (registered Trade Mark), resmethrin, neopynamin registered Trade Mark), and the natural pyrethrins, all commonly known as pyrethroids for example with 5-benzyl-3-furylmethyl alcohol. The 5-benzyl-3-furylmethyl (±) trans-chrysanthemate is especially preferred. Other preferred species include (+) trans allethrin, (+) trans neopynamin, 5-benzyl-3-furylmethyl (±) cis-trans-chrysanthemate, and 5-benzyl-3-furylmethyl (+) cis-chrysanthemate. Other pyrethroids to which the invention is applicable are described in U.S. 3,465,007 (Elliott) and Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 11, pp. 684—7, John Wiley & Sons, New York (1966).

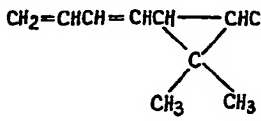
In general, they are esters of acids having the following formula:

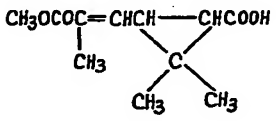


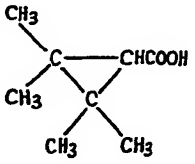
where $R^1$ is methyl or hydrogen, and $R^2$ is methyl, hydrogen, or

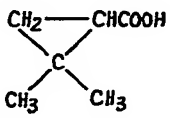


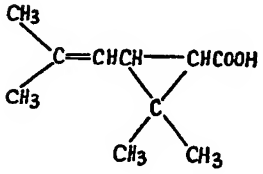
$R^3$ is methyl or hydrogen, $R^4$ is hydrogen, methyl, carbomethoxy, carboethoxy, or halogen, $R^5$ is hydrogen, halogen, alkyl, isoalkyl, alkenyl or isoalkenyl having 1—4 carbon atoms, or $R^4$ and $R^5$ together with the C atom to which they are attached form a cyclopentyl group. Thus, for example, the acid may be any of the following:

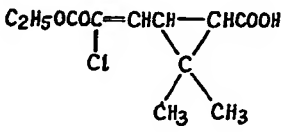


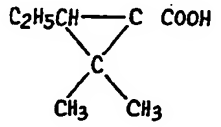


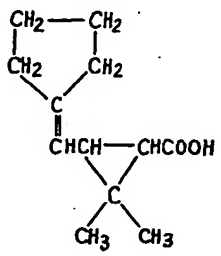


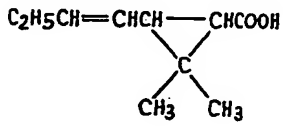


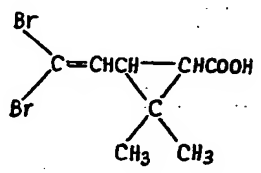


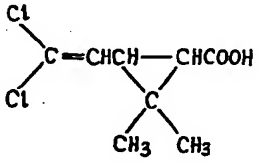






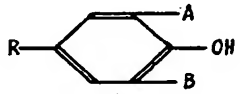




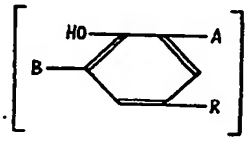


The insecticide compositions of this invention may also contain a synergist. Any of the several well-known synergists may be used, depending upon the particular pyrethroid which is a component of the composition. The synergists include piperonyl butoxide, sulfoxide, sesamex, propyl isome, MKG 264 and tropital. See Kirk-Othmer, supra. These synergists act to enhance considerable the desired activity of the pyrethroids. A characteristic of pyrethrin action on insects is a very rapid knockdown followed by substantial recovery. This recovery is inhibited by the synergist. The amount of synergist, when it is used in the aerosol composition, ranges from one to ten times as much, on a weight basis, as the insecticide.

The antioxidant should as indicated by a relatively non-volatile ortho-substituted phenol. Preferably, the phenol conforms to the structure.



where A is lower alkyl, beta phenethyl or lower alkoxy, B is lower alkyl, alkylene bis-



or hydrogen and R is lower alkyl, amino-substituted lower alkyl, lower alkoxy, or a keto-substituted low alkyl. The term "lower" is used herein to designate an organic group containing fewer than 5 carbon atoms. Those alkyl-substituted phenols having at least 10 carbon atoms are sufficiently non-volatile for the purposes of the invention, and, at the other end of the molecular weight scale, those phenolic compounds having more than 60 carbon atoms per phenolic group are not sufficiently effective to serve the purpose of stabilization herein. These anti-oxidants include BHA (butylated hydroxy anisole), HBT (butylated p-cresol),

Topanol 354 (3,5-di-tertiary butyl 4-hydroxy anisole), ('Topanol' is a Registered Trade Mark), 1,3,5-trimethyl 2,4,6-tris (3,5-di-tertiary butyl 4-hydroxybenzyl) benzene, 2,2-methylene bis (4-methyl 6-tertiary butyl phenol), gamma-tocopherol, propyl gallate, 2,6-di-tertiary butyl alpha dimethylamino-*p*-cresol, 2,5-di-tertiary butyl hydroquinone, guaiaretic acid, Wingstay (Registered Trade Mark) V (the reaction product of equal molar quantities of a *m*-cresol/*p*-cresol mixture, styrene and isobutylene, containing 20—24% of butylated cresols, 23.5—28.5% of styrenated cresols and 42—48% of butylated styrenated cresols) and Zingarone (4-hydroxy 3-methoxy phenyl) ethyl methyl ketone. Other orthosubstituted phenols likewise are contemplated within the scope of the invention. Ordinarily, the ortho-substituent is an alkyl group although it may even be, as in the case of propyl gallate, a second phenolic hydroxyl group.

The relative proportion of such ortho-substituted phenol will range from 0.05% to 2.0%, based on the weight of the insecticide composition. It will be noted that this is a high proportion of antioxidant with respect to the amount of pyrethroid insecticide present in the composition. Ordinarily, at least about 1 part of antioxidant per 5 parts of pyrethroid is present. In some instances, the amount of antioxidant is equal to that of the pyrethroid. A typical formulation includes 0.35% of pyrethroid and 0.20% of antioxidant.

The emulsifying agent is non-ionic. In pressurized sprays the emulsifying agent is non-ionic although an anionic emulsifying agent may also be present, to supplement the effectiveness of the non-ionic emulsifying agent. Ordinary emulsified aqueous sprays utilize anionic emulsifying agents, sometimes in combination with non-ionic emuslifying agents which lend effectiveness in hard water. Suitable non-ionic emulsifiers include polyglycerol oleate, sorbitan monolaurate, ethoxylated mixture of stearyl and cetyl alcohols, glycerol monstearate, sorbitan tristearate, propylene glycol monstearate, diethylene glycol fatty acid ester, polyoxyethylene alkyl phenol, polyoxyethylene monolaurate, and the like. Suitable anionic emulsifying agents include sodium, potassium ammonium and amine salts of hydrophobic carboxylates, sulfates and sulfonates. The amine salts are salts of those alkyl and hydroxyalkyl amines, including primary, secondary and tertiary amines, wherein the alkyl and hydroxyalkyl groups contain fewer than 5 carbon atoms. The hydrophobic carboxylates, sulfates and sulfonates are those containing large, viz., greater than 10 carbon atoms, aliphatic hydrocarbon groups. Illustrative examples of suitable anionic emulsifying agents include: sodium eicosyl sulfate, diethanolamine lauryl sulfate, sodium didodecyl benzene sulfonate, triethanolamine oleate, potassium petroleum sulfonate, etc.

In general, the sulfonates are preferred; they can be defined as R $SO_3$ M where R is a hydrophobic group having at least 10 carbon atoms and M is sodium, potassium, ammonium or lower aliphatic amine (as above). Only as much emulsifier is used as is necessary to sustain a stable emulsion, and this generally is within the limits of from 0.50% to 1.50%, based on the weight of the spray composition.

In the case of pressurized sprays, the propellant preferably is a lower aliphatic hydrocarbon, i.e., a hydrocarbon having 3—6 carbon atoms, viz., propane, butanes, and pentanes. The amount of propellant should be within the range of from 30% to 50% (on a weight basis) of the spray composition.

A corrosion inhibitor may be present, permitting long-term storage in metal containers. Such metal containers are made mainly of tinplate and corrosion inhibitors which are effective to prevent or inhibit the deterioration of tinplate are preferred. These include nitromethane, sodium nitrite, epoxidized soybean oil, sodium benzoate, morpholine, propylene oxide, methyl butynol and the like. When they are used, they should be present in an amount ranging from about 0.01% to about 0.75%, based on the weight of the aerosol composition.

Although the insecticide compositions of the invention are aqueous formulations, they may contain also, in some instances, small proportions of an aliphatic hydrocarbon solvent, i.e., one containing 6—10 carbon atoms, such as isooctane. When it is present, its concentrations should be between 1% and 10%, on a weight basis. It serves to facilitate the incorporation of the pyrethroid insecticide in the emulsion.

A particularly advantageous feature of the insecticide compositions of the invention is their property of flushing out crawling insects such as cockroaches from their hiding places so that they may come into contact with the pyrethroid material.

The insecticide compositions herein are effective not only on ordinary flooring material such as wood or linoleum, but also on glass, unpainted plywood, oil-painted plywood, and latex-painted plywood, although the pyrethrins have a tendency to be absorbed into a latex-painted surface and to lose their residual effectiveness. Apparently their effectiveness is not otherwise affected by the type of surface to which they are applied.

The insecticide composition is as indicated useful against flying insects such as flies and mosquitoes. Knockdown is almost quantitative and % kill within minutes, is almost as good, depending on the particular pyrethroid used. To accomplish both of these objectives, i.e., knockdown and kill, it sometimes is desirable to use two insecticides. Thus, for example, the combination of 5-benzyl-3-furylmethyl (±) trans-chrysanthemate with bioallethrin, natural pyrethrins or neopynamin will achieve both rapid knockdown and a high % kill.

The effectiveness of the pressurized spray compositions herein is shown by the data contained in the following table:

| Pyrethroid Composition (On Glass) | | No. of weeks 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| Example 1. | 0.40% A*<br>0.80% polyglycerol oleate<br>0.38% methyl naphthalene<br>0.50% epoxidized soybean oil<br>67.97% water<br>25.00% isobutane<br>5.00% propane | 100 | 60 | 0 | 0 | | | |
| Example 2. | 0.40% A*<br>0.10% BHA<br>0.75% polyglycerol oleate<br>0.38% methyl naphthalene<br>6.50% light petroleum ether<br>0.50% nitromethane<br>56.42% water<br>35.00% isobutane | 100 | 100 | 100 | 97 | 70 | 26 | 10 |
| Example 3. | 0.40% A*<br>0.20% BHA<br>0.60% polyglycerol oleate<br>0.38% methyl naphthalene<br>0.75% epoxidized soybean oil<br>67.72% water<br>25.00% isobutane<br>5.00% propane | 100 | 100 | 100 | 100 | 90 | 26 | 3 |
| Example 4. | 0.23% A*<br>0.16% bioallethrin**<br>0.10% Wingstay V<br>0.75% polyglycerol oleate<br>0.50% epoxidized soybean oil<br>0.27% methyl naphthalene<br>62.99% water<br>35.00% isobutane | 100 | 100 | 100 | 97 | 93 | 63 | 7 |
| Example 5. | 0.23% A*<br>0.16% bioallethrin**<br>0.20% Wingstay V<br>0.75% polyglycerol oleate<br>0.75% nitromethan<br>0.27% methyl naphthalene<br>67.64% water<br>25.00% isobutane<br>5.00% propane | 100 | 100 | 100 | 100 | 97 | 93 | 56 |

(Continued)

| Pyrethroid Composition (On Glass) | No. of Weeks 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Example 6. 0.25% pyrethrins<br>1.00% piperonyl butoxide<br>0.20% BHT<br>0.75% polyglycerol oleate<br>0.50% light petroleum ether<br>60.80% water<br>25.00% isobutane<br>5.00% propane | 100 | 100 | 100 | 100 | 100 | 100 | 90 |
| Example 7. 0.40% A*<br>0.38% methyl naphthalene<br>19.22% kerosene<br>40.00% trichlorofluoromethane<br>40.00% dichlorodifluoromethane | 100 | 7 | 0 | 0 | | | |
| Example 8. 0.40% A*<br>0.30% BHA<br>0.75% polyglycerol oleate<br>0.75% epoxidized soybean oil<br>0.38% methyl naphthalene<br>17.42% kerosene<br>40.00% trichlorofluoromethane<br>40.00% dicholorodifluoromethane | 100 | 70 | 10 | 0 | | | |
| (On Unpainted Plywood) | | | | | | | |
| Example 9. 0.40% A*<br>0.35% BHA<br>0.38% methyl naphthalene<br>18.87% kerosene<br>40.00% trichlorofluoromethane<br>40.00% dichlorodifluoromethane | 100 | 96 | 26 | 0 | | | |
| Example 10. 0.40%*A*<br>0.20% BHA<br>0.60% polyglycerol oleate<br>0.38% methyl naphthalene<br>0.75% epoxidized soybean oil<br>67.72% water<br>25.00% isobutane<br>5.00% propane | 100 | 100 | 100 | 97 | 84 | 63 | |
| (On Oil-Painted Plywood) | | | | | | | |
| Example 11. 0.40% A*<br>0.30% BHA<br>0.38% methyl naphthalene<br>18.92% kerosene<br>40.00% trichlorofluoromethane<br>40.00% dichlorodifluoromethane | 80 | 20 | 17 | 7 | 0 | | |
| Example 12. 0.40% A*<br>0.10% BHA<br>0.60% polyglycerol oleate<br>0.38% methyl naphthalene<br>0.75% epoxidized soybean oil<br>67.72% water<br>25.00% isobutane<br>5.00% propane | 100 | 100 | 90 | 80 | 67 | 0 | |

(Continued)

| Pyrethroid Composition (On Latex-Painted Plywood) | No. of Weeks 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Example 13. 0.40% A* 0.35% BHA 0.38% methyl naphthalene 18.87% kerosene 40.00% trichlorofluoromethane 40.00% dichlorodifluoromethane | 80 | 50 | 7 | 0 | 0 | | |
| Example 14. 0.40% A* 0.20% BHA 0.60% polyglycerol oleate 0.38% methyl naphthalene 0.75% epoxidized soybean oil 67.72% water 25.00% isobutane 5.00% propane | 100 | 100 | 100 | 100 | 87 | 76 | 0 |

* Chrysanthemic acid ester of (±) trans 5-benzyl-3-furylmethyl alcohol (87.5% active).

** + trans allethrin.

Each of the above pyrethroid compositions is sprayed onto 3 six by six inch plates (glass, unpainted plywood, oil-painted plywood and latex-painted plywood as indicated) so as to deposit a uniform residue of 2.5—6 mg. of toxicant. The surfaces are allowed to dry for at least 24 hours before testing. The test insect is the German roach. The method of testing involves confining ten of these German roaches on each of three plates within circular plastic enclosures two inches high and five inches in diameter, with a copper screen on top of each. The roaches thus have a choice and can avoid the sprayed area if they wish, by climbing up onto this screen. The number of roaches killed within 48 hours is taken as a measure of the effectiveness of the sprayed surface. The test is repeated at weekly intervals to give the data shown above.

It will be noted that wholly oil-based pressurized compositions (Examples 7, 8, 9 and 11) are much less effective than the aqueous-based compositions. This is so even in the case of Examples 8, 9 and 11 which contain antioxidants and emulsifiers. Oil solutions of the ingredients herein likewise are ineffective, i.e., they do not provide extended effectiveness against crawling insects because the pyrethroid ingredient is too readily decomposed.

A typical emulsified aqueous spray composition of the type contemplated herein is prepared from the following concentrate:

60.6% A (as in the table above).
12.0% Wingstay V
3.0% sodium didodecyl benzene sulfonate
3.0% cetyl decaethyleneoxy ethanol
21.4% kerosene

The above concentrate is diluted with 99 volumes of water and may be applied to infested areas by means of a hand-operated spray gun.

Additional test data obtained from similar tests wherein the pyrethroid composition is sprayed onto glass, but wherein the data is collected at slightly irregular intervals, is as follows:

| Pyrethroid Composition | No. of days 7 | 20 | 34 | 41 | 47 |
|---|---|---|---|---|---|
| Example 15. 0.35% B*** 0.60% polyglycerol oleate 0.75% epoxidized soybean oil 68.30% water 25.00% isobutane 5.00% propane | 100 | 0 | — | — | — |
| Example 16. 0.35% B 0.33% Wingstay V 0.60% polyglycerol oleate 0.75% epoxidized soybean oil 67.97% water 25.00% isobutane 5.00% propane | 100 | 100 | 100 | 100 | 20 |
| Example 17. 0.35% C**** 0.60% polyglycerol oleate 0.75% epoxidized soybean oil 68.30% water 25.00% isobutane 5.00% propane | 100 | 40 | — | — | — |
| Example 18. 0.35% C 0.33% Wingstay V 0.60% polyglycerol oleate 0.75% epoxidized soybean oil 67.97% water 25.00% isobutane 5.00% | 100 | 100 | 100 | 60 | 20 |

*** 5-benzyl-3-furylmethyl 2,2,3,3-tetramethyl cyclopropane carboxylate.

**** 5-benzyl-3-furylmethyl-trans(+)-3-(buta-1,3-dienyl)-2,2-dimethyl cyclopropane carboxylate.

In each case above the residue of pyrethroid composition sprayed onto the six by six inch glass plate is 6 mg.

Moreover, the use of emulsified aqueous sprays of the type normally used to control mosquitoes does not serve the purposes of the present invention because such sprays contain too small an amount of pyrethroid. The effectivenes of the insecticide compositions of the present invention lies in the fact that they can be used to deposit a relatively large concentration of pyrethroid and stabilizing agent per unit area of surface and this is not practical with the typical aqueous spray composition. To deposit the required amount of pyrethroid and antioxidant from such an aqueous spray composition would require spraying until the surface is under water.

The invention further provides a method of combating the infestation of crawling or flying insects comprising applying to said insects or to the surface area of such infestation an aqueous spray composition of the invention. The spray composition is preferably applied in such amount as to provide from 5 to 25 mg of pyrethroid per square foot of surface area.

All parts and percentages herein, unless otherwise expressly stated, are by weight.

WHAT WE CLAIM IS:—

1. An aqueous pressurized spray composition comprising from 0.20% to 2.0% by weight of a pyrethroid insecticide, from 0.05% to 2.0% by weight of an ortho-substituted phenol having from 10 to 60 carbon atoms per phenolic group, from 0.5% to 1.5% by weight of a non-ionic emulsifying agent, and from 30% to 50% by weight of a propellant.

2. A composition as claimed in claim 1 wherein the pyrethroid insecticide is an ester of chrysanthemic acid.

3. A composition as claimed in claim 1 wherein the pyrethroid insecticide is one or more natural pyrethrin.

4. A composition as claimed in claim 1 wherein the pyrethroid insecticide is an ester of 5-benzyl-3-furylmethyl alcohol.

5. A composition as claimed in claim 1 wherein the pyrethroid insecticide is 5-benzyl-3-furylmethyl chrysanthemate.

6. A composition as claimed in claim 1 wherein the pyrethroid insecticide is a combination of 5-benzyl-3-furylmethyl chrysanthemate and bioallethrin.

7. A composition as claimed in claim 1 wherein the pyrethroid insecticide is 5-benzyl-3-furylmethyl (±) trans chrysanthemate.

8. A composition as claimed in any one of claims 1 to 7 containing additionally from one to ten parts by weight of a pyrethroid synergist per part by weight of pyrethroid insecticide.

9. A composition as claimed in any one of claims 1 to 8 wherein the ortho-substituted phenol is an ortho-alkyl phenol.

10. A composition as claimed in any one of claims 1 to 8 wherein the ortho-substituted phenol is the reaction produce of equal molar proportions of a *m*-cresol/*p*-cresol mixture, styrene and isobutylene.

11. A composition as claimed in any one of claims 1 to 8 wherein the ortho-substituted phenol is 2,6-di-tertiary butyl alpha dimethylamino-*p*-cresol.

12. A composition as claimed in any one of claims 1 to 11 wherein the propellant is a lower aliphatic hydrocarbon.

13. A composition as claimed in any one of claims 1 to 12 and substantially as hereinbefore described in any one of the Examples.

14. A method of combating the infestation of crawling or flying insects comprising applying to said insects or to the surface area of such infestation an aqueous spray composition as claimed in any one of claims 1 to 13.

15. A method as claimed in claim 14 wherein the aqueous spray composition is applied in such amount as to provide from 5 to 26 mg. of pyrethroid per square foot of surface area.

16. A method as claimed in either claim 14 or claim 15 and substantially as hereinbefore described in any one of the Examples.

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